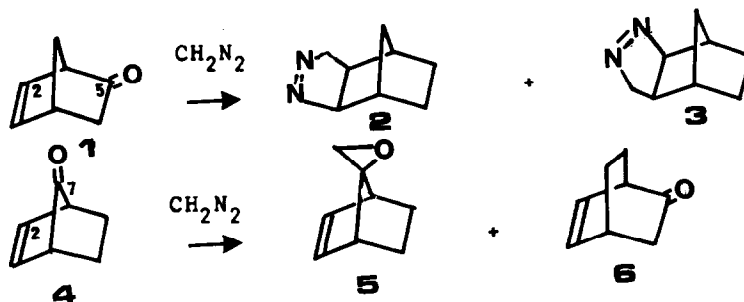


REACTION OF DIAZOALKANES WITH 2-NORBORNEN-7-ONE : DISCREPANCY BETWEEN DIAZOALKANES  $RC(N_2)R'$  AND DIAZOALKANEPHOSPHONATES  $RC(N_2)P(O)(OMe)_2$

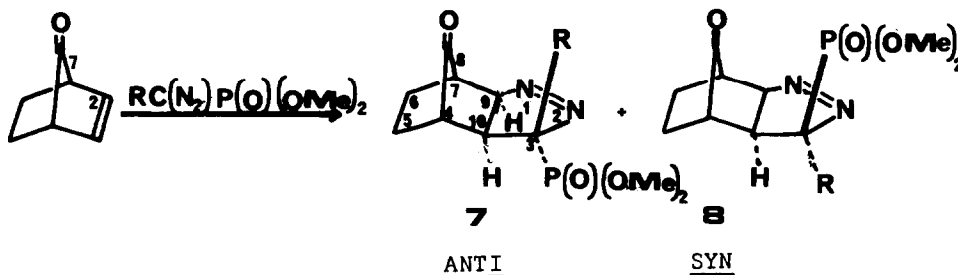
Michel MOREAU, Huguette COHEN and Claude BENEZRA<sup>1</sup>  
 Department of Chemistry, University of Ottawa, Ottawa, Canada KIN 6N5 and  
 Laboratoire de Dermato-Chimie, Associé au CNRS, Université Louis Pasteur,  
 Clinique Dermatologique, Hospices Civils, 67005 STRASBOURG France.

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Depending on the position of the carbonyl group in norbornenones, the reaction with diazomethanes changes dramatically : with 5-norbornene-2-one 1, (dehydronorcamphor), attacks occurs at the double bond, leading to  $\Delta^1$ -pyrazolines 2 and 3, while with 2-norbornene-7-one 4, the epoxide 5 and the ring expanded ketone 6 are the result of attack at the carbonyl carbon<sup>2</sup> :



We have found that reaction of 7-norbornenone 4 with dimethyl aryl- and alkyl diazomethylphosphonates  $RC(N_2)P(O)(OMe)_2$ <sup>3</sup> took a completely different pathway than diazomethane and that the attack was exclusively directed at the double bond, resulting in the formation of both exo-anti - 7 and syn - 8  $\Delta^1$ -pyrazolines, (>80% yield except for  $R = pMeOC_6H_4$ ), according to :



$R = pMeOC_6H_4, p-MeC_6H_4, H, p-CH_3COC_6H_4, CH_3.$

Structures of exo-pyrazolines 7 and 8 were deduced from elemental analyses, infrared (C=O absorption) and n.m.r. spectroscopy [ $J_{9,10} = 0$ ,  $J_{P,10} = 18.5$  Hz in anti, 5.5 in syn<sup>4</sup>]. As in the case of 1,3-dipolar cycloadditions of diazophosphonates to norbornadienes, the anti derivatives predominate.

One possible explanation is that because of the electron-withdrawing group  $P(O)(OMe)_2$ , this diazo carbon is much less nucleophilic than in  $CH_2N_2$  and disfavours nucleophilic addition to  $-C=O$ . When the R group is strongly electron-donating [ $p-MeOC_6H_4$ ], the yield of pyrazoline is poor (about 10% compared to more than 80% in all the other cases). The  $^{13}C$  nmr spectrum of diazoalkanephosphonates<sup>5</sup> support this tentative explanation: the  $^{13}C$  is the most shielded one ( $\delta_{^{13}C}$  relative to  $CS_2$  is 74.5 ppm compared to 65.3 ppm for  $R = C_6H_5$ ).

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#### References and notes

- <sup>1</sup> To whom enquiries concerning this work should be directed at the Strasbourg address.
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